



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 3/085, 21/00	A1	(11) International Publication Number: WO 99/48824 (43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/GB99/00863 (22) International Filing Date: 19 March 1999 (19.03.99) (30) Priority Data: 9805863.9 20 March 1998 (20.03.98) GB (71) Applicant (for all designated States except US): PILKINGTON PLC [GB/GB]; Prescott Road, St. Helens, Merseyside WA10 3TT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BRADSHAW, John, Michael [GB/GB]; 28 Beechfields, Eccleston, Near Chorley, Lancashire PR7 5RE (GB). SMITH, Ian, Heaton [GB/GB]; 24 The Avenue, Rainford, St. Helens, Merseyside WA11 8DT (GB). TORR, Ashley, Carl [GB/GB]; 10 Brooklands, Ormskirk, Lancashire L39 2HD (GB). LYTHGOE, Stanley [GB/GB]; 9 Clovelly Drive, Newburgh, Wigan, Lancashire WN8 7LY (GB). (74) Agents: HALLIWELL, Anthony, Charles et al.; Group Intellectual Property Dept., Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, Lancashire L40 5UF (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CHEMICALLY TOUGHENABLE BORON-FREE FLOAT GLASS COMPOSITIONS (57) Abstract <p>A glass composition capable of being chemically strengthened by ion-exchange within 100 hours to provide a glass with a surface compressive stress of greater than 400MPa and an ion-exchange depth greater than 200 microns comprising: SiO₂ 58 % to 70 % (by weight), Al₂O₃ 5 % to 15 %, Na₂O 12 % to 18 %, K₂O 0.1 % to 5 %, MgO 4 % to 10 %, CaO 0 % to 1 % with the provisos that the total of the Al₂O₃ and MgO is in excess of 13 %, the total of the amounts of Al₂O₃ plus MgO divided by the amount of K₂O is at least 3 and that the sum of the amounts of Na₂O, K₂O and MgO is at least 22 %.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

CHEMICALLY TOUGHENABLE BORON-FREE FLOAT GLASS COMPOSITIONS

The present invention relates to glasses which are capable of being chemically toughened. In particular the present invention relates to glasses which can be chemically toughened and which are primarily, but not essentially, intended for use in aeronautical and automotive vehicles.

In the chemical toughening of glass, the surface of the glass is compressed by the substitution of alkali ions in the surface layers of the glass by heavier, larger ions. This is customarily effected in an ion-exchange bath containing one or more salts of the heavier ions. By so doing, the breaking strength of the glass is increased, thereby permitting the glass to withstand static stresses, such as those experienced in aircraft cockpits or cabins, and more dynamic stresses, such as those encountered if the aircraft strikes a flock of birds.

Chemically strengthenable glasses are well known. Many of these contain significant quantities of lithium. In, for example, United States Patent Specification No. 4156755, there is described and claimed such a glass. However, lithium has the disadvantage of increasing the density of the glass and, in many modern applications for chemically toughened glass, this is not acceptable.

An alternative method of chemically toughening glass if the glass contains sodium ions is to ion-exchange these for potassium ions. Such a method is disclosed in, for example, International (PCT) Patent Application No. WO 94/08910. Such glass has the added advantage that it has a low density of approximately 2.46 in comparison with conventional float glass which has a density of approximately 2.50. Although such patent alleges that no boron need be present in the glass, it is clear that the glass would be more difficult to melt if boron was absent. In fact, this is borne out by the sole example in the patent which discloses a composition containing nearly 3.5% B_2O_3 . Boron oxide lowers the viscosity of the glass. This makes the glass easier to melt and, in theory, easier to refine. Moreover, the combination of, in the context of these glasses, high amounts of both boron and potassium allows the low density to be achieved. However, the use of boron is disadvantageous in that it attacks the silica crowns conventionally used in furnaces.

The use of high quantities of potassium also has drawbacks. In particular, large amounts of potassium cause the production of high viscosity foams early in the melting process. These are very slow to collapse and often lead to silica faults in the finished glass which makes it unacceptable from a commercial viewpoint.

It is desirable if the glasses produced have relatively high strain points so that the ion-exchange can be effected at higher temperatures and the desired level of chemical toughening can be achieved in an economically acceptable time. It is known that the strain point can be raised by increasing the quantities of alumina or zirconia in the glasses. However, these materials are extremely refractory and are difficult to melt in a conventional float furnace within an acceptable time. Alkali metal oxides, such as those of lithium, sodium and potassium help to digest alumina and zirconia but have an adverse effect on the strain point and prevent a high surface compressive stress being achieved during the ion-exchange.

Alkaline earth metal oxides have also been utilised in making glasses which are chemically toughened by ion-exchange. However, these also have drawbacks associated therewith. Zinc oxide is not compatible with the float process, due to the ease with which it is reduced to zinc metal, thereby producing an unacceptable bloom on the glass. Calcium oxide interferes with the sodium/potassium ion-exchange and leads to poor penetration whilst magnesium oxide, particularly in the presence of alumina, normally raises the liquidus temperature of the glass to an unacceptably high level. It will be understood that glasses being manufactured on a float plant should have a positive working range, that is to say, a positive difference between the temperature at which the glass has a viscosity of 10,000 poise and the liquidus, also known as the crystallisation, temperature.

The present invention therefore seeks to provide boron-free glasses having a positive working range, which can be readily melted to float glass standards with respect to the inclusion of bubble and solids and which can be chemically strengthened over a period of less than 100 hours to exhibit a surface stress of at least 400 MPa with a depth of ion penetration greater than 200 microns.

In a subsidiary aspect, the present invention also seeks to provide a glass having a low density. In particular, a low density, in the context of the present invention, is less than 2.48 g/cm³, preferably less than 2.46 g/cm³. This is particularly true if the glass is intended for use in aeronautical applications.

According to the present invention, there is therefore provided a boron-free float glass composition having a positive working range comprising:-

SiO ₂	58% to 70% (by weight)
Al ₂ O ₃	5% to 15%
Na ₂ O	12% to 18%
K ₂ O	0.1% to 5%
MgO	4% to 10%
CaO	0% to 1%

with the provisos that the sum of the Al₂O₃ and MgO exceeds 13%, that the sum of the amounts of Al₂O₃ plus MgO divided by the amount of K₂O exceeds 3 and that the sum of the Na₂O plus K₂O plus MgO exceeds 22%.

We have surprisingly found that the amount of Al₂O₃ is critical. If the amount of Al₂O₃ is less than 5%, insufficient stress can be created when the glass is toughened by ion-exchange but if it is greater than 15%, the glass becomes extremely difficult to melt and causes liquidus problems.

MgO has been found to be a highly desirable component of the glasses of the present invention. It assists in lowering the melting temperature whilst simultaneously not affecting the strain point of the glass. Furthermore, it helps to increase the surface stress of the glass during the ion-exchange process.

Both MgO and Al₂O₃ help to achieve the high surface compressive stress required if the glass is to be used in aeronautical applications. However, when both are present in comparatively high amounts, as in the glasses of the present invention, they can have an adverse effect on the liquidus temperature of the glass.

K₂O poses many problems when melting glass in a float tank. For example, during the melting process, it causes foaming which breaks up into a scum and eventually appears in the finished glass as an inclusion fault. Nevertheless, in the context of the present invention, it is essential to assist in the diffusion of additional potassium ions from the ion-exchange bath so as to achieve sufficiently deep penetration at a reasonable rate. We have surprisingly found that if the amounts of Al₂O₃, MgO and K₂O are as outlined above, the above-mentioned problems do not arise or are at least minimised.

CaO is often used to lower the melting point of glasses. However, its presence in glasses of the present invention lead to low ion penetration during the ion exchange. It is,

therefore, not specifically included in the glasses of the present invention but some CaO may be present as an impurity such as, for example, if the glasses of the present invention are being made in a non-dedicated furnace and CaO was present in the composition previously made in that furnace.

In preferred embodiments of the present invention, other constituents may be present in the composition. For example, iron oxide, which gives glasses containing it a green coloration can be used. If used, the iron will be present in both its ferrous and ferric forms. Ferric iron absorbs radiation in the ultraviolet portion of the electromagnetic spectrum whilst ferrous iron absorbs in the infra-red portion. If iron is to be used, the amount thereof and the ratio of ferrous to ferric iron will be selected in dependence, usually, upon the intended use of the glass. Since iron reduces the visible light transmission of the glass, this is clearly undesirable in aeronautical applications and in communication and detection systems which operate using infra-red beams. In such circumstances, therefore, the amount of iron present is maintained low, that is to say, below 0.2% , preferably below 0.05%. Similarly, the amount of ferrous iron present is maintained as low as possible, that is to say, below 20% and ideally below 15%.

On the other hand, if the glass is intended for use in surface vehicles, the absorption of infra-red radiation and ultraviolet radiation are desirable. In such a case, therefore, the amount of iron present may be as much as 2% or higher and the ferrous level may be as high as 40%. To remove the green coloration, other additives such as cobalt, selenium and/or nickel may be included in the composition. If it is desired to improve the ultraviolet absorption of the glass, additives such as cerium or titanium may be included in the composition.

Float glasses are conventionally refined using sulphate, generally identified as SO_3 , and carbon. However, the usual amounts of these materials added to the composition of the present invention causes excessive foaming . We have found that the glass may be readily refined if the amount of SO_3 present in the batch is limited to 0.1% to 0.4%.

The potassium salt used for the ion-exchange may be any suitable salt such as the sulphate, the chloride or mixtures thereof. However, for their general ease of use and for their melting range the nitrates are preferred. The ion-exchange medium may be formed into

a paste with an inert medium such as oxides of iron, titanium or silicon as is well known in the art. As is also known per se, the ion-exchange may be accelerated, if desired, by the application of an electric field to the process.

Polished samples of the glasses were strengthened by ion-exchange in a chemical bath containing 99.5% KNO_3 and 0.5% silicic acid at temperatures ranging from 400°C to 460°C for periods of from 25 hours to 240 hours. Temperatures of below 400°C may be used but, if a large ion-exchange bath is being employed, there is the possibility of the temperature in localised regions dropping below the melting point of the potassium nitrate. Similarly, temperatures of over 500°C may be employed but, at this temperature level, the potassium nitrate begins to decompose which can have deleterious effects on the quality of the glass and may also release noxious fumes. Following immersion, the glasses were allowed to drain for 30 minutes and were then cooled in air to ambient temperature. Residual salt was washed from the glass and the surface stress and the depth of the compressive layer were measured using a Differential Stress Refractometer. The data was modified to take into account changes in the refractive index of the composition and of the stress optical coefficient. Birefringence was related to applied stress, the comparison being made with a conventional soda-lime-silica glass as made by the float process. The data obtained were combined to predict how long the ion-exchange treatment would need to be continued at a selected temperature to achieve a pre-determined surface stress and compressive depth. Compositions having the desired predicted properties were then prepared as samples for strength testing, were treated for the predicted length of time and were then strength tested to destruction.

The invention will be further described, by way of example, with reference to the following non-limitative Examples:-

TABLE (continued)

Glass No.	Fe ³⁺	(Al ₂ O ₃ +MgO)	(Al ₂ O ₃ +MgO)/K ₂ O	Time taken to achieve 400 MPa surface stress and 200 microns compressive depth (hours)	Temperature required to achieve 400 MPa surface stress and 200 microns compressive depth (°C)	Surface stress (MPa) achieved at 430°C after 81 hours
1	18	16.6	3.4	66 to 71	437 to 438	420
2	19	15.4	3.4	101 to 102	434	444
3	10	15.0	3.3	16 to 31	471	515
4	19	14.4	3.3	72 to 74	438 to 439	439
5	19	17.0	4.4	19 to 31	462 to 470	512
6	16	15.5	4.0	42 to 61	445 to 455	434
7	19	19.0	4.9	11 to 13	504 to 507	670
8	20	15.3	3.9	48 to 57	439 to 443	409
9	17	16.2	4.5	48 to 58	437 to 441	407
10	18	16.1	4.5	35 to 39	446 to 448	441
11	18	18.6	5.3	2 to 12	493 to 464	477
12	17	15.6	4.9	35 to 37	455 to 456	454
13	18	17.0	5.3	84 to 94	443 to 444	505
14	19	16.3	6.5	97 to 105	423 to 425	396
15	18	16.4	8.2	32 to 61	442 to 459	435
16	19	16.8	28.0	81 to 108	427 to 433	414
17	-	16.2	-	114 to 121	424 to 426	408
18	36	16.0	4.4	16 to 19	473 to 477	474
19	23	15.9	4.5	20 to 21	475	563
20	22	15.6	4.5	39 to 48	457 to 459	577
21	18	16.0	4.4	41 to 64	440 to 453	426
22	17	16.0	4.4	17 to 22	465 to 470	513
23	-	16.0	4.4	45 to 52	438 to 441	383
24	-	25.0	41.7	10 to 11	500 to 510*	442
25	-	12.8	3.6	147 to 149	407 to 408	364
26	-	10.7	3.0	898 to 1332	351 to 357	342
27	-	11.9	2.0	84 to 88	450 to 451	496
28	-	5.0	8.3	3896 to 4337	400 to 401	462
Note * denotes temperature restricted to 510°C as salt would decompose at higher temperatures						

TABLE (continued)

Glass No.	Property					T (Liquidus) (°C)	Density (g cm ⁻³)	Thermal expansion coefficient (100-300°C) (×10 ⁻⁷ /°C)
	Temp. at 10 ^{2.5} poise (°C)	Temp. at 10 ^{4.0} poise (°C)	Annealing point (°C)	Strain point (°C)				
1	1362	1067	-	-		920	2.480	-
2	1362	1068	-	-		970	2.469	-
3	1364	1072	572	539		1056	2.468	103.8
4	1388	1081	-	-		920	2.463	-
5	1382	1085	-	-		1070	2.475	-
6	1431	1112	553	513		950	2.457	-
7	1478	1157	583	545		1006	2.463	100.5
8	1438	1112	549	511		912	2.458	102.5
9	1427	1103	560	524		939	2.560	106.0
10	1432	1110	571	534		-	2.456	-
11	-	-	585	546		-	2.457	105.6
12	1422	1098	567	531		925	2.455	100.5
13	1374	1078	-	-		1043	2.472	-
14	1436	1114	579	541		-	2.455	-
15	1438	1106	579	544		903	2.454	-
16	1437	1119	-	-		-	2.453	99.5
17	1442	1125	587	553		-	2.454	-
18	1432	1116	563	526		-	2.469	-
19	1427	1111	-	-		909	2.476	-
20	1413	1106	565	527		948	2.495	-
21	1422	1105	-	-		-	2.470	-
22	-	-	-	-		-	2.476	-
23	1439	1110	569	534		960	2.457	104.0
24	1368	1092	613	577		1150	2.504	108.5
25	1418	1101	-	-		-	2.442	-
26	1393	1080	-	-		-	2.436	-
27	1346	1043	548	513		-	2.456	98.5
28	1335	1035	554	523		1000	2.502	89.5

In the Examples given above, Examples 1 to 16 inclusive show basic compositions in accordance with the present invention. In Examples 18 and 19, the effect of adding iron oxide (Fe_2O_3) is shown. In Example 20, the iron content has been raised to 3.8% and it can be seen that the chemical strengthening properties have not been impaired but the density of the glass has increased. Examples 21 and 22 show that the addition of 1% by weight of, respectively TiO_2 and ZrO_2 do not adversely affect the chemical strengthening properties but, like high quantities of iron, do increase the density of the glass. Example 23 includes phosphorus and although it can be seen that the chemical strengthening properties are not affected, phosphorus has high corrosive effects on the refractories of the furnace. Example 24 shows that a higher content of Na_2O and Al_2O_3 substantially increase the density of the glass and mean that it has a negative working range. This Example is, therefore, a comparative Example.

Examples 17, 25, 26, 27 and 28 are further comparative Examples. Example 25 shows that if the aluminium oxide plus magnesium oxide content is lower than 13%, the time required to strengthen the glass to a desired depth is substantially increased. Example 26 shows that the same problem is encountered if the aluminium oxide content is less than 5%. Example 17 shows that the presence of less than 0.1% potassium oxide permits the desired chemical strengthening to be achieved but, again, the time taken to achieve this is long.

Example 27 is a commercial ion-exchange glass containing boron which, as aforementioned, is not used in the present invention due to the necessity of providing a dedicated furnace with boron resistant refractory materials. Finally, Example 28 is a standard window float glass.

CLAIMS

1. A boron-free float glass composition capable of being chemically strengthened over a period of less than 100 hours to exhibit a surface stress of at least 400 MPa with a depth of ion penetration greater than 200 microns comprising:-

SiO ₂	58% to 70% (by weight)
Al ₂ O ₃	5% to 15%
Na ₂ O	12% to 18%
K ₂ O	0.1% to 5%
MgO	4% to 10%
CaO	0% to 1%

with the provisos that the sum of the Al₂O₃ and MgO exceeds 13%, that the sum of the amounts of Al₂O₃ plus MgO divided by the amount of K₂O exceeds 3 and that the sum of the Na₂O plus K₂O plus MgO exceeds 22%.

2. A composition as claimed in Claim 1 additionally containing Fe₂O₃ in an amount of from 0.2% to 4% by weight, the ferrous state being at least 20%.
3. A composition as claimed in Claim 1 additionally containing Fe₂O₃ in an amount of less than 0.2% by weight.
4. A composition as claimed in Claim 3 additionally including cerium oxide in an amount of from 0.05% to 0.5% by weight.
5. A composition as claimed in Claim 3 or 4 wherein the ferrous state is less than 20%.
6. A composition as claimed in any one of Claims 1 to 5 additionally containing TiO₂ in an amount of up to 1% by weight.
7. A composition as claimed in any preceding Claim additionally containing sulphate in an amount of from 0.1% to 0.4% by weight.

8. A composition as claimed in any one of Claims 2 to 7 additionally including a colorant for neutralising the green colour produced by the Fe_2O_3 .
9. A composition as claimed in Claim 8 wherein the colorant is selected from cobalt oxide, nickel oxide or selenium or mixtures thereof.
10. A composition as claimed in any preceding claim in which the Al_2O_3 is present in an amount in excess of 6% by weight and the MgO is present in an amount of from 4% to 8% by weight.
11. A composition as claimed in any one of Claims 1 to 9 in which the MgO is present in an amount in excess of 8% by weight and the Al_2O_3 is present in an amount of from 5% to 9% by weight.
12. A composition as claimed in any preceding Claim in which the K_2O is present in an amount of from 0.5% to 3.5% by weight and the Al_2O_3 is present in an amount of from 5.5% to 11% by weight.
13. A composition as claimed in Claim 1 substantially as hereinbefore described with reference to the foregoing Examples.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00863

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C3/085 C03C21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 196 16 633 C (SCHOTT GLASWERKE) 7 May 1997 see claims; examples 3,4; table 3 ---	1-13
A	SOVIET INVENTIONS ILLUSTRATED Section Ch, Week 8541 Derwent Publications Ltd., London, GB; Class H01, AN 85-254649 XP002106746 -& SU 1 146 288 A (GLASS RES INST) , 23 March 1985 see abstract; example 4 ---	1-13
A	US 4 055 703 A (RINEHART DALE W) 25 October 1977 see column 13, line 11 - line 65 see claims --- -/-	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

21 June 1999

Date of mailing of the international search report

01/07/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kuehne, H-C

INTERNATIONAL SEARCH REPORT

Intern: at Application No

PCT/GB 99/00863

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 772 135 A (HARA M ET AL) 13 November 1973 see claims; example 2 ---	1-13
P,A	US 5 804 317 A (CHARRUE HERVE) 8 September 1998 see column 5, line 25 - column 6, line 22 see claims -& FR 2 704 852 A ---	1-13
P,A	FR 2 761 978 A (SAINT GOBAIN VITRAGE) 16 October 1998 see claims; example 4 ---	1-13
A	WO 94 08910 A (SAINT GOBAIN VITRAGE) 28 April 1994 cited in the application see claims; figures ---	1-13
A	US 4 156 755 A (RINEHART DALE W) 29 May 1979 cited in the application see claims -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/00863

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19616633 C	07-05-1997	JP 10072238 A US 5895768 A	17-03-1998 20-04-1999
US 4055703 A	25-10-1977	US 4015045 A US 4053679 A US 4119760 A	29-03-1977 11-10-1977 10-10-1978
US 3772135 A	13-11-1973	BE 753189 A DE 2034393 A FR 2051664 A GB 1322228 A	16-12-1970 28-01-1971 09-04-1971 04-07-1973
US 5804317 A	08-09-1998	FR 2704852 A DE 69402661 D DE 69402661 T EP 0649393 A ES 2102225 T WO 9426675 A JP 8500812 T	10-11-1994 22-05-1997 16-10-1997 26-04-1995 16-07-1997 24-11-1994 30-01-1996
FR 2761978 A	16-10-1998	EP 0914298 A WO 9846537 A	12-05-1999 22-10-1998
WO 9408910 A	28-04-1994	FR 2697242 A CN 1089926 A DE 69303619 D DE 69303619 T EP 0665822 A ES 2092335 T US 5773148 A	29-04-1994 27-07-1994 14-08-1996 06-03-1997 09-08-1995 16-11-1996 30-06-1998
US 4156755 A	29-05-1979	NONE	